



Influence of H₂, CO₂ and H₂O on the activity and deactivation behavior of Au/CeO₂ catalysts in the water gas shift reaction at 300 °C

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ARTICLE INFO

Article history:

Received 20 August 2009

Received in revised form 29 November 2009

Accepted 9 December 2009

Available online 16 December 2009

Keywords:

Water gas shift reaction
High temperature reaction
Reaction kinetics
Deactivation
Au catalysts
Au/CeO₂
Realistic reformat
DRIFTS

ABSTRACT

The effect of H₂, CO₂ and H₂O on the activity, stability and deactivation behavior of an oxidatively (O400) and a reductively (H400) pretreated 4.5 wt.% Au/CeO₂ catalyst in the water gas shift (WGS) reaction at 300 °C was studied by kinetic and spectroscopic measurements, using different gas mixtures, going stepwise from idealized to a semi-realistic reaction atmosphere. The results were compared with data for the WGS reaction determined under similar reaction conditions at a lower reaction temperature of 180 °C [Y. Denkwitz, A. Karpenko, V. Plzak, R. Leppelt, B. Schumacher, R.J. Behm, J. Catal. 246 (2007) 74]. The formation/removal of adsorbed reaction intermediates and side products (surface carbonates, formates, OH_{ad}, CO_{ad}) was followed by *in situ* IR spectroscopy (DRIFTS). Variation of the reaction gas mixture led to significant effects on the initial activity and the stability of the catalysts, which depend also on the pre-treatment of the catalysts. The resulting trends are compared with those obtained for reaction at 180 °C, consequences for the reaction mechanism and for applications in fuel gas processing at medium temperatures will be discussed.

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1. Introduction

As a key reaction for enhancing the hydrogen yield from industrial processes such as steam reforming of natural gas or the gasification of carbon-rich materials [1–3], the water gas shift (WGS) reaction is of considerable interest for providing high-grade hydrogen for possible future hydrogen energy systems. The fuel gases resulting from the primary processes such as steam reforming contain in general about 1–10% CO, which for application in low-temperature fuel cells such as Polymer Electrolyte Fuel Cells (PEFCs) has to be reduced to below 10 ppm to avoid poisoning of the fuel cell anode catalyst by strongly adsorbed CO_{ad} species [1,4–6]. In technical applications, Cu/ZnO/Al₂O₃ catalysts are commonly used in the ‘low temperature’ WGS reaction (200–250 °C) [7–9], but ceria-supported noble metal catalysts have been increasingly investigated as an alternative to CuZnO catalysts in applications for fuel processing [3,8–17]. Especially Au/CeO₂ has turned out to be a very active catalyst in the low-temperature WGS reaction [17–32]. The technical application of Au/CeO₂ catalysts in the WGS reaction is hindered, however, by their pronounced deactivation, which was

attributed to a number of different effects, including (i) metal particle growth [13], (ii) loss of surface area [22], (iii) over-reduction of support [33], and/or, more recently, (iv) partial detachment of the Au nanoparticles from the support [34], or (v) blocking of active centers by adsorbed surface formate or carbonate species, which are formed as reaction intermediates and/or by-products during the reaction [16,23,26]. The latter interpretation was supported by the experimental observation of obvious correlations between deactivation behavior and the build-up of these surface species upon varying the composition of the reaction gas [29,31]. For instance, for reaction at 180 °C, the presence of H₂ or CO₂ in the reaction gas mixture significantly lowered the activity or the stability of the Au/CeO₂ catalyst, respectively [29,31]. This behavior was related to the formation of thermally stable monodentate carbonates, acting as reaction-inhibiting spectator species. The formation of monodentate carbonates was enhanced by CO₂, whereas H₂ accelerates their reactive removal, most likely by reaction to formates [29,31].

If deactivation is dominated by the accumulation of surface formates and carbonates, one might envision that their build-up may decrease with higher temperatures, due to their increasing thermal decomposition, which in turn would reduce the catalyst deactivation. If at the same time Au particle sintering is not accelerated under these conditions, and furthermore the rate of the WGS reaction increases due to thermal activation, it would be tempting to use Au/CeO₂ catalysts at elevated temperatures, in particular in applications where higher temperatures are of

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interest from technical reasons. Therefore, we had started a systematic study of the WGS reaction behavior over Au/CeO₂ catalysts at higher reaction temperatures around 300 °C, investigating the activity and stability of the catalyst, the build-up of reaction intermediates and side products on the catalyst surface, and their role in the reaction, as well as the influence of the catalyst pre-treatment on these properties at this reaction temperature. Results obtained during reaction in idealized reformat (1 kPa CO, 2 kPa H₂O, rest N₂) were reported recently [32]. We now extended this study, focusing on the influence of typical components in more realistic reformat gases such as H₂, CO₂ and higher amounts of CO and/or H₂O. This was done by systematically varying the reaction atmosphere, going stepwise from idealized reformat up to close-to-realistic gas compositions. The activity and deactivation as well as the build-up of intermediates and by-products were followed in combined kinetic and *in situ* IR spectroscopic measurements. To gain further information on the effect of catalyst pre-treatment, all measurements were performed on two differently pre-treated catalysts, which were pre-treated either oxidatively (O400) or reductively (H400) at 400 °C prior to the catalytic measurements. The results are compared with those already reported earlier for reaction at lower temperature (180 °C), using the same Au/CeO₂ catalyst and the same reaction atmospheres [29,31], and with data obtained for reaction at 300 °C in idealized reformat [32].

2. Experimental

Most of the experimental details were reported already previously [32]. Therefore, we will summarize here only the main aspects.

2.1. Catalyst preparation

The Au/CeO₂ catalysts were prepared by a precipitation-deposition method. The supporting CeO₂ (HSA 15, Rhodia, calcined in air at 400 °C for 4 h) was re-dispersed in water at 60 °C, and subsequently gold precursor (HAuCl₄·3H₂O, 99.5%, grade for analysis, Merck) was added drop-wise, while adjusting the pH value to between 5 and 6 by adding Na₂CO₃ solution. A more detailed description of the catalyst preparation procedure can be found in refs. [26,35]. The amount of gold on the support was determined to 4.5 wt.% Au, using inductively coupled plasma-atom emission spectroscopy (ICP-AES). The BET surface area of the

catalyst, as determined by N₂ adsorption measurements, was 188 m² g⁻¹. Before the catalytic measurements, the catalyst was first heated in N₂ (20 N ml min⁻¹) to 400 °C, followed by either calcination in oxidative atmosphere (10% O₂/N₂—O400) or reduction in 10% H₂/N₂ atmosphere (H400) at 400 °C for 30 min (20 N ml min⁻¹). Subsequently, the catalyst was cooled down in 20 N ml min⁻¹ N₂ to the reaction temperature of 300 °C.

2.2. Activity measurements

For the kinetic measurements, we used a quartz tube micro reactor (i.d. 4 mm) located in a ceramic tube furnace. The measurements were performed at atmospheric pressure under differential reaction conditions, using typically 60–80 mg diluted catalyst powder. To limit the conversion to below 20%, the catalyst was diluted with α-Al₂O₃, which is inactive for the WGS reaction under present reaction conditions (dilution between 1:200 and pure catalyst, depending on the reaction atmosphere and pre-treatment). All reaction measurements were carried out with a gas flow of 60 N ml min⁻¹. The different reaction gas mixtures used for the present study include: idealized reformat; H₂O-rich idealized reformat, CO₂-containing idealized reformat, H₂-rich idealized reformat, CO₂-containing H₂-rich idealized reformat, and finally the more realistic reformates mixtures 1/4 realistic reformat and 1/2 realistic reformat (compositions see Table 1). The names of the gas mixtures follow those used in our previous study on reaction at 180 °C [29,31]. All gas mixtures were prepared by mass flow controller (Hasting HFC-202), using high purity gases from Westphalen (CO 4.7, N₂ 6.0, H₂ 5.0, and CO₂ 5.0). Water vapor was added to the gas stream using a saturation unit with controlled temperature. The composition of the incoming and effluent gas flow was analyzed by on-line gas chromatography (Chrompack CP9001), using H₂ as a carrier gas. Further details on the kinetic measurements are given in reference [36].

2.3. Infrared measurements

In situ infrared (IR) investigations were performed in a reaction cell for diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) (Harricks, HV-DR2) and a Magna 560 spectrometer (Nicolet) equipped with a liquid N₂ cooled MCT narrow band detector. In these measurements, the gas flows were controlled in the same way as for the activity measurements (Hasting HFC-202),

Table 1
Reaction rates during WGS reaction at 300 °C over 4.5 wt.% Au/CeO₂ catalysts in different reaction gas mixtures.

Reaction gas mixture	Gas composition (kPa)	O400			H400		
		Initial rate (mol g _{Au} ⁻¹ s ⁻¹)	Rate after 1000 min (mol g _{Au} ⁻¹ s ⁻¹)	Relative rate after 1000 min (%)	Initial rate (mol g _{Au} ⁻¹ s ⁻¹)	Rate after 1000 min (mol g _{Au} ⁻¹ s ⁻¹)	Relative rate after 1000 min (%)
Idealized reformat	(1 CO, 99 N ₂ (dry)); +2H ₂ O	2.3 × 10 ⁻³	6.3 × 10 ⁻⁴	27	3.4 × 10 ⁻⁴	1.9 × 10 ⁻⁴	57
H ₂ O-rich idealized reformat	(1 CO, 99 N ₂ (dry)); +5H ₂ O	2.6 × 10 ⁻³	9.1 × 10 ⁻⁴	35	5.4 × 10 ⁻⁴	3.1 × 10 ⁻⁴	57
H ₂ -rich idealized reformat	(1 CO, 99 N ₂ (dry)); +10H ₂ O	2.8 × 10 ⁻³	1.4 × 10 ⁻³	53	6.3 × 10 ⁻⁴	4.4 × 10 ⁻⁴	68
	(1 CO, 99 H ₂ (dry)); +2H ₂ O	4.8 × 10 ⁻⁴	1.8 × 10 ⁻⁴	38	1.7 × 10 ⁻⁴	1.33 × 10 ⁻⁴	79
	(1 CO, 99 H ₂ (dry)); +10H ₂ O	7.2 × 10 ⁻⁴	3.2 × 10 ⁻⁴	45	2.3 × 10 ⁻⁴	1.9 × 10 ⁻⁴	84
CO ₂ -containing idealized reformat	(1 CO, 1 CO ₂ , 98 N ₂ (dry)); +2H ₂ O	1.03 × 10 ⁻³	4.4 × 10 ⁻⁴	43	2.5 × 10 ⁻⁴	1.7 × 10 ⁻⁴	67
CO ₂ + H ₂ -rich idealized reformat	(1 CO, 1 CO ₂ , 98H ₂ (dry)); +10H ₂ O	2.9 × 10 ⁻⁴	1.1 × 10 ⁻⁴	37	3.2 × 10 ⁻⁵	2.5 × 10 ⁻⁵	78
1/4 realistic reformat	(1 CO, 4.2 CO ₂ , 75.2 N ₂ , 19.6 H ₂ (dry)); +5H ₂ O	3.6 × 10 ⁻⁵	2.2 × 10 ⁻⁵	61	3.4 × 10 ⁻⁵	3.1 × 10 ⁻⁵	88
1/2 realistic reformat	(2 CO, 8.4 CO ₂ , 50.5 N ₂ , 39.1 H ₂ (dry)); +10 H ₂ O	8.8 × 10 ⁻⁵	5.7 × 10 ⁻⁵	65	4.1 × 10 ⁻⁵	3.8 × 10 ⁻⁵	91

with a total flow rate of 60 N ml min^{-1} . Prior to the infrared investigations, the catalysts were pre-treated in the same way as for the kinetic measurements. About 20 mg of pure catalyst on a bed of about 60 mg pure $\alpha\text{-Al}_2\text{O}_3$ were used. Typically, 400 scans (acquisition time 3 min) at a nominal resolution of 8 cm^{-1} were added for one spectrum. The intensities were evaluated in Kubelka–Munk units, which are linearly related to the adsorbate concentration on the catalyst surface [37] (for exceptions see ref. [38]). Background subtraction was performed using a spectrum recorded in a stream of N_2 at the reaction temperature, directly after catalyst conditioning. To correct for variations in the reflectivity of the respective catalysts, the spectra were scaled to similar intensities at 3000 cm^{-1} , where the background intensity does not interfere with any other signals and does not change during the reaction. The gas phase CO signal was removed by subtraction of the corresponding spectral region ($2040\text{--}2240 \text{ cm}^{-1}$) from spectra recorded under the same reaction conditions on an inert $\alpha\text{-Al}_2\text{O}_3$ support in CO containing atmosphere from those obtained on the Au/CeO₂ catalyst.

3. Results and discussion

3.1. Activity measurements

3.1.1. Effect of the water content in idealized reformate

In a first set of measurements, we studied the influence of water on the activity and deactivation behavior of the catalyst in the WGS reaction, by varying the amount of water vapor (2, 5, and 10 kPa) in the idealized reformate (see Table 1). The decay of the activity with time on stream is shown in Fig. 1a (O400 catalyst) and Fig. 1b (H400 catalyst). Generally, the initial and final activity was higher

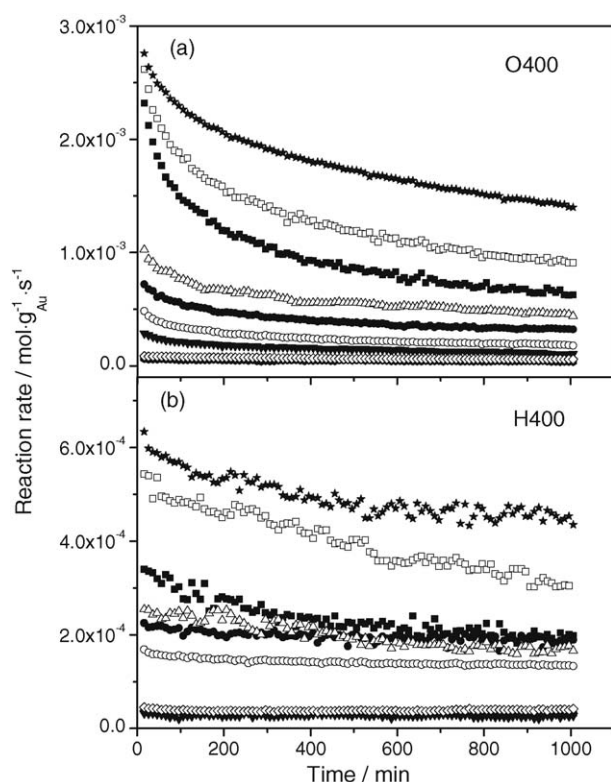


Fig. 1. Initial activity and deactivation of Au/CeO₂ catalysts in the WGS reaction in different reaction gas mixtures (a) O400 and (b) H400. Gas mixtures (■) idealized reformate, (□) 5% H₂O-rich idealized reformate, (★) 10% H₂O-rich idealized reformate, (○) H₂-rich idealized reformate, (●) 10% H₂O–H₂-rich idealized reformate, (△) CO₂-containing idealized reformate, (▼) CO₂ + H₂-rich idealized reformate, (●) 1/4 realistic reformate, and (◇) 1/2 realistic reformate (gas compositions see Table 1).

on the O400 catalyst than on the H400 catalyst under the same reaction conditions. In all cases, the activity decreased approximately exponentially with time, by between 47% and 73% for the O400 and 32–43% for the H400 catalyst over 1000 min on stream.

Obviously, the amount of water in the feed gas has a significant effect on the activity and stability of the respective catalysts, and the same is true also for the pre-treatment. While the influence of water on the initial activity of the O400 catalyst was negligible (initial rates vary from 2.3×10^{-3} (2 kPa H₂O) to $2.8 \times 10^{-3} \text{ mol g}_{\text{Au}}^{-1} \text{ s}^{-1}$ (10 kPa H₂O)), a relatively strong effect was found for the H400 sample. For these catalysts, the initial activity in the 2 kPa H₂O containing gas mixture ($3.4 \times 10^{-4} \text{ mol g}_{\text{Au}}^{-1} \text{ s}^{-1}$) was half compared to that in the gas mixture with 10 kPa of water ($6.3 \times 10^{-4} \text{ mol g}_{\text{Au}}^{-1} \text{ s}^{-1}$). This effect can possibly be correlated to the presence of different amounts of adsorbed carbonates species after pre-treatment in H₂ (high amount) or O₂ (low amount), which will be discussed in more detail in Section 3.2 (see also ref. [32]).

The water concentration had a significant effect on the catalyst stability and deactivation behavior in the WGS reaction. The stability increased with increasing water content, going from 73% deactivation (final activity 27% of the initial activity) at 2 kPa water content to about 47% deactivation in the 10 kPa water containing reaction gas mixture for the O400 catalyst. For the H400 catalyst, in contrast, the presence of higher water contents during the reaction had a much lower effect on the deactivation, which decreased only by about 10% as the water content changed from 2 to 10 kPa, from 43% to 32%.

Our results agree well with other literature data obtained on comparable catalysts. In previous studies of the WGS reaction on Au/CeO₂ at lower temperatures, the effect of water on the WGS activity in idealized reformate was explored by Leppelt et al., who found the activity to increase with increasing water content (see next section) [26]. The effect of water on the deactivation behavior in idealized reformate has not been investigated previously. Including also Pt/CeO₂ catalysts, Luengnarumitchai et al. [13] reported that the water vapor content significantly enhanced the catalytic performance of various catalysts (1% Pt/CeO₂ and 1% Au/CeO₂ pretreated in O₂ at 110 °C/2 h; 3% Au/Fe₂O₃ pre-treated in 1% H₂ in He (250 °C/12 h); gas mixture 4% CO in He, 2.6 or 20% H₂O (120–360 °C)). The maximum CO conversion over 1% Pt/CeO₂ increased from 18% to 85% at 360 °C, as the water vapor in the stream was increased from 2.6% to 20%. The effect was less pronounced for 1% Au/CeO₂ and 3% Au/Fe₂O₃ catalysts, where the increased water content (20%) increased the maximum conversion from 8% to 15% and from 33% to 53%, respectively.

3.1.2. Reaction order of water in idealized reformate

More quantitatively, the influence of water in idealized reformate is described by the reaction order for water, which was determined by varying the water concentration stepwise from 2 to 10 kPa in idealized reformate mixture (1 kPa CO, 99 kPa N₂ (dry), 2–10 kPa H₂O). The reaction rates were measured after 1000 min reaction initially and then at least 60 min equilibration per data point. The results are plotted in Fig. 2a and b for the O400 and the H400 catalyst, respectively.

Different from the absolute activities, the pre-treatment procedure does not seem to play an important role for the H₂O reaction order. For both catalysts, the O400 and the H400 catalyst, we obtain a value of 0.2 ± 0.02 , from the slopes of the lines in Fig. 2. This is in good agreement with the value of 0.5 determined on a 2.6 wt.% Au/CeO₂ catalyst for reaction at 180 °C in comparable gas mixtures (idealized reformate, 0.7–10 kPa H₂O, balance N₂) [26]. Considering also other ceria-supported metal catalysts, Koryabkina et al. [39] reported a reaction order of 0.4 for H₂O in realistic reformate (7 kPa CO, 10–46 kPa H₂O, 37 kPa H₂, 8.5 kPa CO₂, balance Ar) for the WGS reaction at 240 °C on a 8 wt.% CuO/CeO₂ catalyst. Hilaire et al. [11] derived a reaction order of 0.5 for H₂O in the WGS reaction in idealized reformate on Pd/

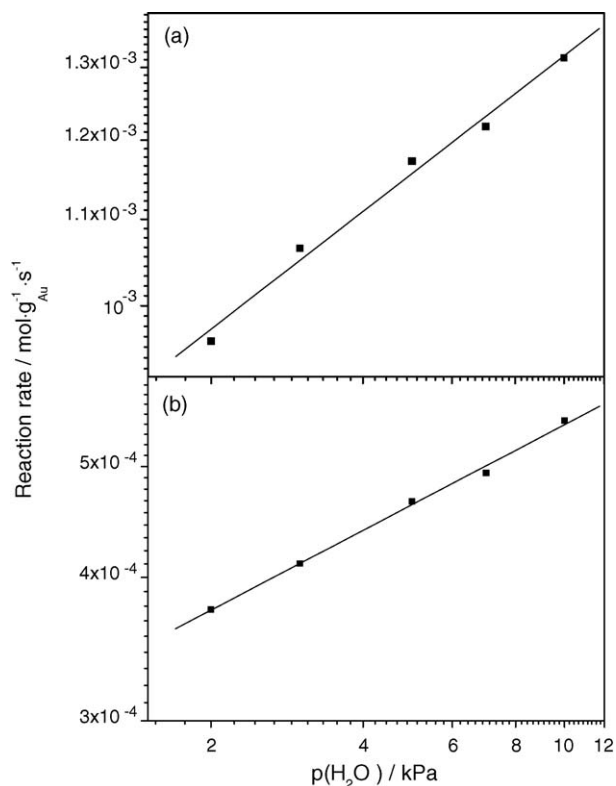


Fig. 2. Determination of the reaction order of water (2–10 kPa H_2O , 1 kPa CO, balance N_2) at 300 °C and in a gas flow of 60 N ml min^{-1} (rate after 1000 min reaction initially and at least 60 min equilibration per data point) (a) O400 and (b) H400.

CeO_2 at 200 °C (3.2 kPa CO, 4.6–263 kPa H_2O , balance He). Bunluesin et al. [10] determined a reaction order of 1 for H_2O using different supported metal-on-ceria catalysts (Pd, Pt and Rh) and gas mixtures containing 2.7 kPa CO and varied amounts of water (not mentioned, rest N_2) in the WGS reaction at 300 °C. For other catalysts (iron based catalysts, CuO/ZnO, $\text{Ni}(\text{OH})_2$ on C), reaction orders for water were reported to be in the range of 0.5–0.7 [40–42]. In total, the reaction order of water seems to be rather little affected by the nature of the support and of the active metal used in these studies. Tentatively, we relate this to water adsorption and dissociation on the oxide support or the active oxide component, respectively.

3.1.3. Effect of additional components in idealized reformate

In this section, we describe the effect of adding other components to the *idealized reformate* mixture on the activity and stability of the two differently pre-treated catalysts (O400 and H400), see Fig. 1 and Table 1. First, the addition of 1 kPa CO_2 to the *idealized reformate* reaction gas mixture (CO_2 -containing *idealized reformate*) leads on the one hand to a decrease of the initial activity to about 45% (O400) and 74% (H400) of their initial values in *idealized reformate*, respectively. On the other hand, the stability was increased compared with that in *idealized reformate*, with the deactivation over 1000 min on stream decreasing to 57% and 33% for the O400 and H400 catalysts, respectively.

In H_2 -rich *idealized reformate*, where the N_2 was replaced by hydrogen, the initial activity drops significantly on the O400 catalyst, reaching only about 23% of that in *idealized reformate*. On the other hand, also the deactivation decreased from 73% to 62% after 1000 min reaction. In the case of the H400 catalyst, the loss of initial activity was less pronounced. It decreased to half of the value in *idealized reformate*. For the stability, the positive effects were substantial; the deactivation after 1000 min on stream decreased from 43% in *idealized reformate* to 21% in H_2 -rich *idealized reformate* (see Table 1).

For comparison with *idealized reformate* (see previous sections), we also explored the influence of increased water contents on the activity/stability of the O400 and H400 catalysts in the WGS in H_2 -rich *reformate*, adding 10 kPa of water instead of 2 kPa to the dry gas mixture. Similar to the observations in *idealized reformate*, the increased amount of water led to an increase in both the initial activity and stability. While the initial activity increased by 33% and 26% for the O400 and H400 catalysts relative to that in H_2 -rich *reformate*, respectively; the deactivation after 1000 min on stream was only 55% and 16%, compared to 62% and 21% in H_2 -rich *reformate* containing only 2 kPa H_2O .

To identify the combined effect of CO_2 and H_2 on the catalytic behavior, we used a reaction gas mixture containing both gases (1 kPa CO, 1 kPa CO_2 , 98 kPa H_2 (dry)); +2 kPa H_2O). In this reaction atmosphere and at 300 °C, the reaction equilibrium was shifted to the reverse water gas shift, leading to an increase in CO content. In order to shift the reaction back into the forward reaction, the water content was increased to 10 kPa (CO_2 + H_2 -rich *idealized reformate*). This resulted in a considerable loss of activity for both catalysts, to 13% (O400) and 9% (H400) of that in *idealized reformate*. These were the lowest activities for both catalysts measured in all *idealized reaction gas mixtures*. The stabilities were comparable to those in *idealized reformate*, with deactivations of 63% and 22% over 1000 min on stream.

It should be noted that upon the addition of CO_2 and/or H_2 one would expect the global (net) reaction rate to decrease because of increasing contributions from the reverse WGS (RWGS) reaction. Since on the other hand, the presence of these components is likely to change also the surface composition of the catalyst and hence the reaction constant of the forward reaction, k_1 , these contributions can not easily be calculated from k_1 and the (tabulated) equilibrium constant of the WGS/RWGS reaction, K_{eq} (see also ref. [43]). Therefore, we will also in these cases use the measured global rates in the discussion of the reactivity.

The results presented for the different *idealized gas mixtures* can be summarized as follows:

1. The initial and steady-state activities were always higher for the oxidatively (O400) than for the reductively (H400) pre-treated catalysts. On the other hand, the H400 catalyst showed a higher stability than the O400 catalyst in the same reaction gas mixtures. Nevertheless, the steady-state activities were below those of the O400 catalysts.
2. Independent of the pre-treatment procedure used, the initial and steady-state activity decreased in the order:

H_2O -rich *idealized reformate* \approx *idealized reformate*
 $>$ CO_2 -containing *idealized reformate* $>$ H_2 -rich *idealized reformate* $>$ CO_2 + H_2 -rich *idealized reformate*

3. The stability depends sensitively on the pre-treatment of the catalysts. For the O400 catalyst, the stability decreased in the order:

H_2O -rich *idealized reformate* (10 kPa H_2O) $>$ H_2 -rich *idealized reformate* (10 kPa H_2O) \approx CO_2 -containing *idealized reformate* $>$ H_2 -rich *idealized reformate* (2 kPa H_2O) \approx CO_2 + H_2 -rich *idealized reformate* \approx H_2O -rich *idealized reformate* (5 kPa H_2O) $>$ *idealized reformate*

For the H400 catalyst, it decreased in the order:

H_2 -rich *idealized reformate* (10 kPa H_2O) $>$ H_2 -rich *idealized reformate* (2 kPa H_2O) \approx CO_2 + H_2 -rich *idealized reformate* $>$ H_2O -rich *idealized reformate* (10 kPa H_2O) \approx CO_2 -containing *idealized reformate* $>$ H_2O -rich *idealized reformate* (5 kPa H_2O) \approx *idealized reformate*

Independent of the pre-treatment, the lowest stability (highest deactivation) of the catalysts was observed in *idealized reformate*, which on the other hand also showed the highest initial activity. Adding water to the *idealized reformate* has little effect on the initial activity (small increase in activity), but significantly reduces the deactivation of the O400 catalyst, making this the most reactive reaction atmosphere under steady-state conditions. For the H400 catalyst, the activity increase is stronger, but the effect on the deactivation is less pronounced. Addition of H₂ to the *idealized reformate* reduces the initial activity, independent of the catalyst pre-treatment, but also reduces the deactivation, with the loss in initial activity being less pronounced on the H400 than on the O400 catalyst. Finally, addition of CO₂ also reduces the initial activity of the O400 catalyst, but less pronounced than H₂. Considering, however, that the amount of CO₂ (1 kPa) added was much less than that of H₂ (99 kPa), the effect of CO₂ is clearly more intense. The deactivation is reduced for both catalysts.

Next, we compare the results presented above with data reported previously for the WGS reaction at 180 °C on three different Au/CeO₂ catalysts, one with oxidative pre-treatment (2.8 wt.% Au/CeO₂ catalyst, oxidative pre-treatment at 400 °C (O400) [24]) and two with reductive pre-treatment (4.5 wt.% Au/CeO₂ catalyst, reductive pre-treatment at 230 °C (H230) [29] and 2.8 wt.% Au/CeO₂ catalyst, reductive pre-treatment at 200 °C (H200) [24,31]). The related reaction data are compiled in Table 2. First of all, the initial and steady-state activities obtained at 300 °C on the oxidatively pre-treated catalyst (O400) are significantly higher than those obtained on a comparable (2.8 wt.% Au/CeO₂) O400 catalyst at 180 °C in *idealized reformate*, with the initial activity increasing by a factor of 6 [24] (see Table 2). The deactivation after 1000 min on stream, however, also increased substantially, from 14% at 180 °C to 73% in O400 at 300 °C, leaving the final intensities only double as high at 300 °C than at 180 °C.

For catalysts pre-treated at 400 °C in reductive atmosphere (H400), we only can compare the reaction behavior in *idealized reformate* at 180 °C (2.8 wt.% Au/CeO₂ catalyst) [24] with our present data. Going from 180 to 300 °C reaction temperature, both the initial activity and the deactivation increased, from 2.0×10^{-4}

to 3.4×10^{-4} and from 23% to 43% [24] (see Table 2). The increase of the initial activity with temperature, however, is much less than for the O400 catalyst, and also the increase in deactivation with temperature is less pronounced.

The trends of the changes in activity and stability induced by the composition of the reaction atmosphere at 180 and 300 °C are harder to compare, since in previous studies we had only used catalysts which were reductively pre-treated at 200 or 230 °C. (These lower pre-treatment temperatures made no sense in the present study, since in that case the reaction temperature would be higher than the conditioning temperature.) Therefore, the difference in pre-treatment conditions will affect not only the activity/stability in a given gas mixture, but possibly also the sensitivity and response towards the reaction gas composition. For instance, in *idealized reformate* the initial activity at 180 °C decreased to 30% when comparing a H200 and a H400 pre-treated catalyst (see Table 2) [24].

For a H230 catalyst, which was used in a previous study on the influence of the reaction atmosphere and its different components for the WGS reaction at 180 °C [29], the initial and steady-state activities decreased in the order (see Table 2):

idealized reformate > CO₂-containing idealized reformate
> H₂-rich idealized reformate ≈ CO₂ + H₂-rich idealized reformate

while the stability (deactivation over 1000 min reaction) decreased in the order:

idealized reformate > H₂-rich idealized reformate >
CO₂-containing idealized reformate > CO₂ + H₂-rich idealized
reformate (2 kPa H₂O)

Comparable results were reported also by Karpenko et al. for a H200 pre-treated catalyst, who found the initial activity and also the stability (deactivation over 1000 min reaction) to decrease in the order (see Table 2) [31]:

idealized reformate > H₂-rich idealized reformate > CO₂
+ H₂-rich idealized reformate (2 kPa H₂O).

Comparison with the data for the H400 catalyst in the present study does not show clear trends, neither for the activity nor for the deactivation behavior. For instance, in *idealized reformate*, the

Table 2

WGS reaction rates at 180 °C over various Au/CeO₂ catalysts after different pre-treatment in different reaction gas mixtures.

Catalyst	Reaction gas mixture	Gas composition (kPa)	Pre-treatment	Reference	Initial rate (mol g _{Au} ⁻¹ s ⁻¹)	Rate after 1000 min (mol g _{Au} ⁻¹ s ⁻¹)	Relative rate after 1000 min (%)
4.5 wt.%Au/CeO ₂	Idealized reformate	(1 CO, 99 N ₂ (dry)); +2H ₂ O	H230	[29]	4.5×10^{-4}	3.6×10^{-4}	79
2.6 wt.%Au/CeO ₂			H200	[26]	2.2×10^{-4}	1.6×10^{-4}	79–85
2.8 wt.%Au/CeO ₂			H200	[31]	8.1×10^{-4}	6.0×10^{-4}	74
2.7 wt.%Au/CeO ₂			H200	[24]	8.1×10^{-4}	6.0×10^{-4}	74
2.7 wt.%Au/CeO ₂			H300	[24]	5.0×10^{-4}	6.8×10^{-4}	75
2.7 wt.%Au/CeO ₂			H400	[24]	2.1×10^{-4}	1.6×10^{-4}	77
2.7 wt.%Au/CeO ₂			N200	[24]	8.1×10^{-4}	5.2×10^{-4}	64
2.7 wt.%Au/CeO ₂			O200	[24]	8.0×10^{-4}	5.8×10^{-4}	72
2.7 wt.%Au/CeO ₂			O300	[24]	4.1×10^{-4}	3.0×10^{-4}	72
2.7 wt.%Au/CeO ₂			O400	[24]	3.7×10^{-4}	3.2×10^{-4}	86
2.8 wt.%Au/CeO ₂	H ₂ -rich idealized reformate	(1 CO, 99 H ₂ (dry)); +2H ₂ O	H200	[31]	2.3×10^{-4}	1.7×10^{-4}	72
4.5 wt.%Au/CeO ₂			H230	[29]	2.2×10^{-5}	1.7×10^{-5}	77
4.5 wt.%Au/CeO ₂	CO ₂ -containing idealized reformate	(1 CO, 1 CO ₂ , 98 N ₂ (dry)); +2H ₂ O	H200	[29]	3.0×10^{-4}	1.9×10^{-4}	63
2.8 wt.%Au/CeO ₂	CO ₂ + H ₂ -rich idealized reformate	(1 CO, 1 CO ₂ , 98 H ₂ (dry)); +2H ₂ O	H200	[31]	2.3×10^{-5}	1.4×10^{-5}	62
4.5 wt.%Au/CeO ₂			H230	[29]	2.3×10^{-5}	1.3×10^{-5}	56
4.5 wt.%Au/CeO ₂	1/4 realistic reformate	(1 CO, 4.2 CO ₂ , 75.2 N ₂ , 19.6 H ₂ (dry)); +5H ₂ O	H230	[29]	1.9×10^{-5}	8.8×10^{-6}	46
4.5 wt.%Au/CeO ₂	1/2 realistic reformate	(2 CO, 8.4 CO ₂ , 50.5 N ₂ , 39.1 H ₂ (dry)); +10H ₂ O	H230	[29]	5.9×10^{-5}	2.3×10^{-5}	38

initial activity was highest at 180 °C reaction temperature, but lowest at 300 °C. For H_2 -rich idealized reformat, the changes in activity and stability were only small when going from 180 to 300 °C. At both temperatures, the addition of H_2 leads to a decrease of the activity compared to idealized reformat [24,31]. At 180 °C, also the stability is little affected by the addition of H_2 , while at 300 °C the catalyst is stabilized (lower deactivation compared to idealized reformat).

Finally, we compare the trends for the O400 catalyst at 300 °C reaction temperature with those of the reductively pre-treated catalyst (H230, H200) at 180 °C. Interestingly, the decrease of activity followed the same order in both cases. On the other hand, there are significant differences in the stability behavior. For instance, for reaction at 300 °C, the lowest stability was observed in idealized reformat, while for reactions at 180 °C both catalysts (H230, H200) showed the highest stability in this reaction mixture. Considering the distinct effects of the pre-treatment on the activity and stability of the Au/CeO₂ catalyst for the WGS reaction observed in the present work, the agreement in the activity trends between an O400 catalyst at 300 °C reaction temperature and an H200 catalyst at 180 °C should not be over-interpreted. Definitely, the variation of the reaction gas composition, reaction temperature, and catalyst pre-treatment all go along with considerable changes in the surface composition of the catalysts under reaction conditions, which will affect the reaction behavior and which will be discussed in more detail in Section 3.2.

The significant changes in the deactivation behavior and in the response to adding other components to the idealized reformat upon increasing the reaction temperature from 180 to 300 °C may result not only from changes in the catalyst surface composition, but also from a change in the reaction mechanism. Burch [9] had proposed that the prevalent reaction pathway for the WGS reaction over Au/CeO₂ catalysts (and previously also for other catalysts such as Pt/ZrO₂ [44]) will change with temperature, from the formation and decomposition of formate, carbonate or carboxylate species as dominant pathway at lower temperatures to a redox mechanism, involving reduction and re-oxidation of the ceria support, at higher temperatures [9]. Such change in reaction mechanism would of course also affect the influence of co-reactants in the reaction gas mixture. In our previous paper on the 300 °C WGS reaction in idealized reformat [32], we concluded that the mechanism of the WGS reaction on a Au/CeO₂ catalyst does not change in idealized reformat between 180 and 300 °C reaction temperature, based on the small change in apparent activation energies at lower and higher temperatures. By comparison with earlier work [26], a reaction path proceeding via formate formation and decomposition was favored as dominant mechanism [32]. For the more complex reaction atmospheres investigated in the present study, such change in mechanism, which would result, e.g., from a less pronounced rate increase of the reaction pathway dominant at 180 °C compared to a competing pathway, can not be ruled out, although we also have no evidence for supporting this.

It should be noted that for reaction on an Au/CeZrO₄ catalyst at lower temperatures, between 100 and 150 °C, Meunier et al. had shown that formation and decomposition of IR visible formates contributes little to the reaction [17]. Since, however, the contribution of this pathway increased considerably with temperature, this may well be compatible with significant contributions from the formate pathway under present reaction conditions, at 300 °C (for a more detailed discussion see further below). For reaction on Cu surfaces, theoretical studies favored reaction via a carboxyl intermediate [45,46], the relevance of these findings for Au/CeO₂ catalyst, however, needs to be proven.

Comparison of the kinetic data obtained at 300 °C in idealized gas mixtures and their variation in different reaction gas mixtures

or, for the same reaction atmosphere, upon increasing the reaction temperature over comparable ranges (180 → 300 °C), with other data on Au catalysts is limited by the small amount of relevant data and by the diversity in the reaction conditions employed in different studies of the WGS reaction (for an overview see ref. [9]). Since the composition of the gas phase in these studies often resembled more that of the realistic reformates discussed in the following section, we will make this comparison in the following section.

3.1.4. More realistic reformat (quarter and semi-realistic reformat)

Finally, we investigated the activity and stability of 4.5 wt.% Au/CeO₂ catalysts at 300 °C in 1/4 and 1/2 realistic reformat (gas composition see Table 1). The deactivation behavior in the more realistic reformates followed the same trend as in idealized reformat, with a significant decay of the activity with time independent of the pre-treatment conditions (H400, O400). The reaction time of 1000 min was sufficient to reach approximately steady-state conditions. The activity was generally higher at the higher reaction temperature of 300 than at 180 °C [29], but, as mentioned before, the difference in pre-treatment has to be considered as well (O400/H400 at 300 °C vs. H200 at 180 °C), which for reaction in idealized reformat at 180 °C was significant [24].

On the O400 catalyst, reaction in 1/4 realistic reformat resulted in the lowest initial and final activities of all gas mixtures, while on the H400 catalyst, the activities in 1/4 and 1/2 realistic reformates are also low, but still slightly higher than in CO₂ + H_2 -rich idealized reformat. Comparing the more realistic reformat mixtures with idealized reformat, the stability was improved independent of the pre-treatment conditions. In 1/2 realistic reformat, we obtained the highest stability among all reaction mixtures studied, with deactivations of 35% (O400) and 9% (H400), respectively. In realistic reformates, the deactivation is significantly lower at 300 °C than at 180 °C, while for all idealized reformates the situation was opposite, with a distinctly higher deactivation at 300 °C than at 180 °C. Possible reasons for this behavior will be discussed in more detail later. Nevertheless, because of the low initial activities in the realistic reformat mixtures, the final (steady-state) activity was at the lower end of all reaction gas mixtures.

Comparing with reaction at 180 °C on the H230 catalyst, the relative activities in the two realistic gas mixtures behaved similar, with a higher activity in 1/2 realistic reformat at 180 °C and at 300 °C (both for O400 and H400). The trend of the stability, in contrast, was reversed at 300 °C compared to reaction at 180 °C, with a higher stability (less pronounced deactivation) in 1/4 realistic reformat at 180 °C (H230), while at 300 °C the stability was higher in 1/2 realistic reformat (H400 and O400). As discussed before, the reversed order of the stability may at least partly be related to the differences in the pre-treatment, and thus to differences in the catalyst surface composition prior to the reaction, though other effects can not be ruled out.

Finally, we compared the trends in the influence of the reaction atmosphere on the activity and stability of the O400 and H400 catalysts during high temperature reaction with the limited set of existent data. Concentrating on Au/CeO₂ catalysts and high reaction temperatures (≥ 300 °C), the following studies are relevant: Fu et al. [22] determined a reaction rate of $4.2 \times 10^{-3} \text{ mol g}_{\text{Au}}^{-1} \text{ s}^{-1}$ at 300 °C using a more realistic gas mixture (11% CO, 7% CO₂, 26% H₂O, 26% H₂, 4.7 wt.% Au/CeO₂, calcination at 400 °C), which is still higher than that reported in our study. Under those reaction conditions, they found an almost constant activity over 120 h on stream [18,22]. Andreeva et al. [20] reported that Au/CeO₂ catalysts containing 1–5 wt.% Au are very stable during the WGS reaction over a wide temperature range (reaction temperature 140–350 °C, 1 h reduction

in 1% H₂/Ar at 100 °C, gas mixture 5 kPa CO, 30 kPa H₂O and rest Ar). They assumed that deactivation caused by Au nanoparticle sintering is counteracted by a re-dispersion of the Au particles during the reaction. On the other hand, there are a number of studies reporting a pronounced deactivation of Au/CeO₂ or related catalysts during the WGS reaction under comparable reaction conditions. Kim and Thompson [23] observed a fast and considerable loss in catalyst activity (about 50%) for reaction at 240 °C on a 5 wt.% Au/CeO₂ catalyst (reductive pre-treatment in 4% H₂/N₂ for 4 h at 400 °C; reaction mixture: 10 kPa CO, 22 kPa H₂O, 6 kPa CO₂, 43 kPa H₂ and 19 kPa N₂), and explained this by an increasing surface blocking by surface carbonate and/or formate species, which are produced during the WGS reaction. This interpretation is similar to our current understanding of the deactivation, which we attribute mainly to the accumulation of stable monodentate surface carbonate species both at lower (180 °C) [29,31] and higher (300 °C) reaction temperatures [23,32] (see Section 3.2). Comparable results were reported by Luengnarumitchai et al. [13], who observed a strong deactivation (83%) after 48 h WGS reaction at 360 °C in 2% CO and 20% H₂O on a 1 wt.% Au/CeO₂ catalyst (calcination at 500 °C in air for 5 h), while on Pt/CeO₂ they found no significant deactivation. They related this deactivation to a Au particle growth during the reaction, from 4 to 5.5 nm based on XRD and TEM measurements. A similar result was reported by Wang et al. [47], who compared the deactivation of Pt/ceria and Pd/ceria catalysts during the WGS reaction (3.3 kPa H₂O, 3.3 kPa CO, rest He; 250 °C), and related the observed decrease in activity (conversion decreased from 23% to 18%) to a loss of metal surface area due to the growth of metal particles in CO. Because of the rather small increase in Au particle size (from 2.9/2.6 to 3.6/3.2 nm for O400 and H400, respectively) during the WGS reaction at 300 °C on Au/CeO₂ (idealized reformat) [32], Au particle growth can essentially be ruled out as main reason for catalyst deactivation in our measurements. Furthermore, since the loss in surface area upon particle growth from 4.0 to 5.5 nm in ref. [13] would not be sufficient to explain a loss of activity by 83% just by geometric arguments, this would require other physical effects to explain the strong particle dependence.

Zalc et al. [33] assumed a very different mechanism for deactivation of a Pt/CeO₂ catalyst (total pressure 304 kPa: CO₂: 12.5 kPa, H₂: 63 kPa, H₂O: 125 kPa, N₂: 63 kPa, CO: 42 kPa, pre-calcined at 500 °C, reaction at 250 °C). They proposed that an irreversible over-reduction of the ceria support in the H₂-rich feed gas is responsible for the deactivation. This assumption was, however, disclaimed by other authors [47], who found no evidence for deactivation of the catalyst by heating in pure H₂ at 400 °C, and there might even be an increase in the conversion after the H₂ treatment for WGS reaction on a 1 wt.% Pd/ceria at 350 °C. Kim and Thompson [23] also reported the absence of any measurable effects in the deactivation behavior when replacing 43% He in the gas mixture by H₂ (reaction gas mixture 10 kPa CO, 22 kPa H₂O, 6 kPa CO₂, 43 kPa H₂ and 19 kPa N₂, 240 °C). Finally, Goguet et al. proposed for 2% Au/CeZrO₄ catalysts that the deactivation is caused by partial detachment of the Au nanoparticles from the support surface, driven by hydrolysis ($T < 250$ °C) or thermally ($T > 250$ °C) [34].

In total, a consistent explanation of the different results is hardly possible because of the very different reaction conditions (temperature, gas composition, catalyst pre-treatment). Most data agree, however, that under present reaction conditions Au particle sintering is not important for catalyst deactivation, and also irreversible over-reduction of the ceria appears to be little likely, leaving increasing blocking of the catalyst surface by adsorbed reaction side products (surface carbonates) as the most likely origin for catalyst deactivation also under present reaction conditions, at 300 °C in increasingly realistic reaction gas mixtures (for reaction at 180 °C see [29]).

3.2. Accumulation of adsorbed reaction intermediates during the WGS reaction

The accumulation of adsorbed reaction intermediates and side products on the different catalysts (O400 and H400) during the WGS reaction was followed by *in situ* IR spectroscopy (DRIFTS) measurements, using the same reaction conditions as applied for the kinetic measurements. During the first 10 min, spectra were recorded every 12 s, co-adding 20 scans. Subsequently, 400 scans were co-added per spectrum, resulting in 3 min measurement time per spectrum.

Selected spectra from these time sequences, recorded 24, 48 s, 1, 5, 10, 30, 60, 120, 360, 600 and 1020 min after the reaction was started, are presented in Fig. 3 (O400) and Fig. 4 (H400). Each set of spectra shows the entire spectrum (bottom) as well as details of the regions characteristic for OCO vibrations (middle right), for CO_{ad}/CO₂ (middle left), for C–H stretch vibrations (top right), and for O–H stretch vibrations (top left). If necessary, different magnifications were used for the CO₂ signal and the CO_{ad} signal, respectively. For a quantitative evaluation of the reaction induced modifications in the adlayer, we plotted the temporal evolution of the formate peak intensities (2828–2832 cm⁻¹) and of several peaks in the OCO bending region in Fig. 5. The latter include the bidentate carbonate related peak at 1281–1310 cm⁻¹, the monodentate carbonate related peak at 1397–1420 cm⁻¹ (H400)/1365–1369 cm⁻¹ (O400), the carbonate related peak at 1520–1522 cm⁻¹ (O400 catalysts), and finally the formate related peak at 1582–1590 cm⁻¹ (for assignments see ref. [48]). The CO₂ intensity was not plotted since CO₂ is present in many of the reaction gas mixtures, and the quantitative evaluation of the CO_{ad} peak is hindered for the H400 catalysts by its overlap with an electronic transition donor levels located near the conduction band such as Ce³⁺ or oxygen vacancies [49]. The influence of the water content in *idealized reformat* on the amount of surface carbonate and formate species and on gaseous CO₂ formation under steady-state conditions is illustrated in Fig. 6. The intensities shown in Figs. 5 and 6 were corrected for reaction induced changes in the reflectivity (see Section 2). In the following, the different vibrational regions will be described separately.

3.2.1. OH region (3800–3300 cm⁻¹)

Different bands in the region of OH vibrations were assigned to monodentate OH_{ad} groups (3710 cm⁻¹), bidentate OH_{ad} groups (3671 cm⁻¹), tridentate OH_{ad} groups (3500 cm⁻¹) and bridged OH_{ad} group (3646–3649 cm⁻¹) on the ceria support, respectively, for both O400 and H400 catalysts [50,51]. The origin of another band at 3588 cm⁻¹, which was observed in all reaction atmospheres independent of the pre-treatment procedure and whose intensity did not change significantly during the reaction, has not yet been clarified. This band was also detected during the WGS reaction at 180 °C on these Au/CeO₂ catalysts [26,29].

The only major difference between the O400 and H400 catalysts in this region is that in *idealized reformat* reaction mixtures on the O400 catalysts, the band for bridged OH_{ad} group at 3649 cm⁻¹ starts to develop at the beginning of the reaction (after 48 s), while on the H400 catalyst sample and for the other reaction mixtures on the O400 catalyst, this band existed already at the beginning of the reaction. Since in the background spectra recorded before starting the reaction this peak is not present on the O400 catalyst, these species must be formed very quickly on these catalysts, within the first 40 s of the reaction. Overall, this band is more pronounced in more reductive atmospheres. Apparently, it is related to a reduced state of the support [24,32].

Otherwise, no new peaks appeared during the reaction. Only the intensities of the different OH_{ad} species changed slightly

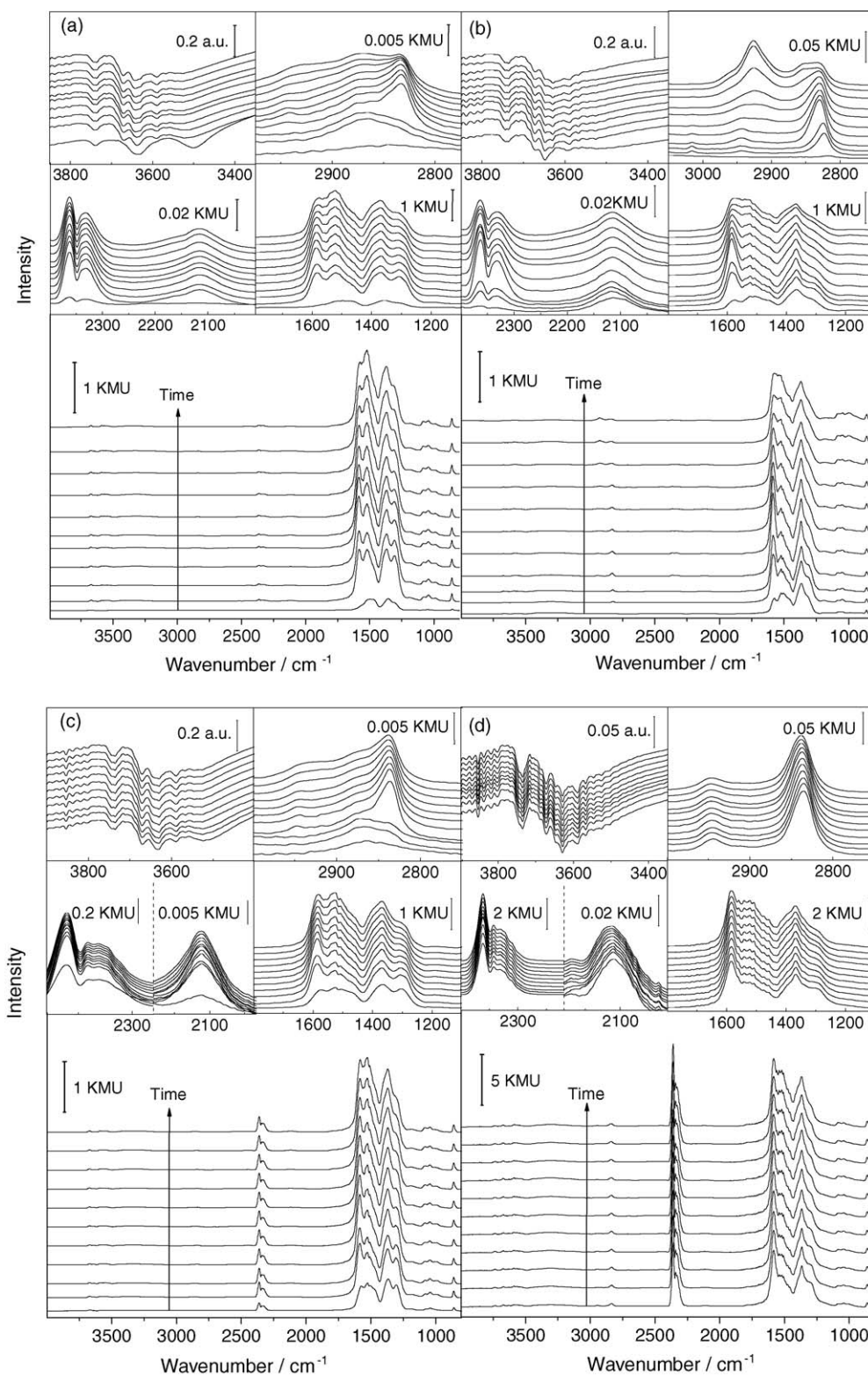


Fig. 3. Sequence of DRIFT spectra recorded during 1000 min WGS reaction in different gas mixtures at 300 °C on a 4.5 wt.% Au/CeO₂ catalyst after oxidative pretreatment (O400). (a) Idealized reformat, (b) H₂-rich idealized reformat, (c) CO₂-containing idealized reformat, and (d) 1/2 realistic reformat (gas compositions see Section 2.1). The IR-regions are displayed in the following order from bottom to top: full spectrum (bottom), OCO region (middle right), CO_ad/CO₂ region (middle left), C–H region (top right) and O–H region (top left). The spectra displayed were recorded after 24, 48 s, 1, 5, 10, 30, 60, 120, 360, 600 and 1020 min.

with time. For all reaction mixtures and independent of the catalyst pre-treatment, the peak at 3649 cm⁻¹ grows at the beginning of the reaction, reaching a maximum after about 10 min reaction time, and then decreased slowly up to the end of

the reaction, with a final value of about 85–90% of the maximal intensity. This peak was assigned recently to bridged hydroxyl groups, which were considered to be an educt for formate formation [26,51,52].

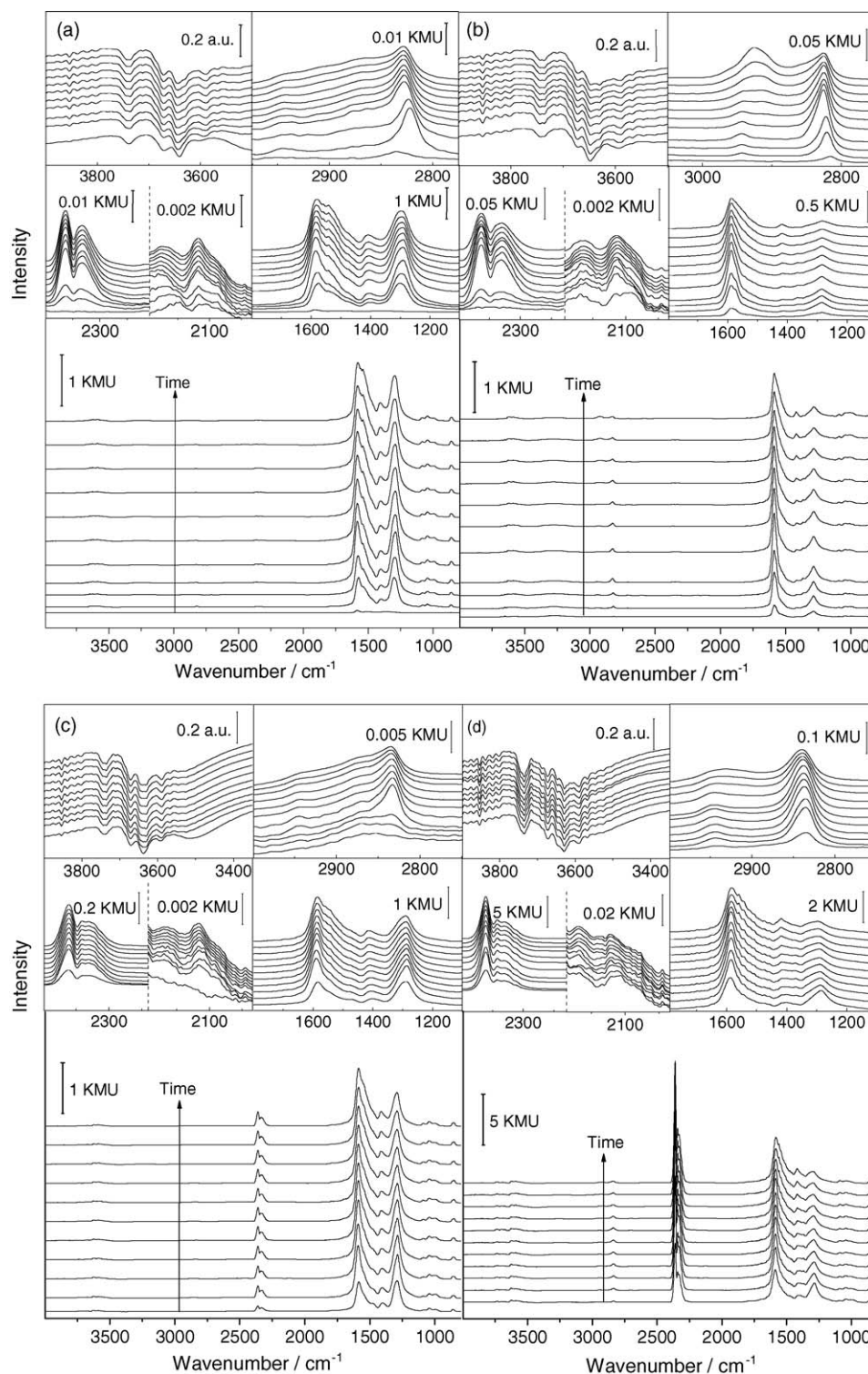


Fig. 4. Sequence of DRIFT spectra recorded during 1000 min WGS reaction in different gas mixtures at 300 °C on a 4.5 wt.% Au/CeO₂ catalyst after reductive pretreatment (H400). (a) Idealized reformate, (b) H₂-rich idealized reformate, (c) CO₂-containing idealized reformate, and (d) 1/2 realistic reformate (gas compositions see Section 2.2). The IR-regions are displayed in the following order from bottom to top: full spectrum (bottom), OCO region (middle right), CO_{ad}/CO₂ region (middle left), C–H region (top right) and O–H region (top left). The spectra displayed were recorded after 24, 48 s, 1, 5, 10, 30, 60, 120, 360, 600 and 1020 min.

3.2.2. C–H region (3000–2800 cm⁻¹)

More direct information on the formation of formate species during the WGS reaction is obtained from the C–H stretch vibrations in this region (bidentate formates at 2826–2836 cm⁻¹, bridge-bonded formates at 2941 cm⁻¹), where the exact position depends on the pre-treatment and the gas mixture [50,52,53]. These C–H signals are accompanied by OCO bending

vibrations at ~1585 cm⁻¹ (antisymmetric mode, on O400 and H400 catalyst in all gas mixtures) and 1373 cm⁻¹ (symmetric mode, more clearly on O400 catalysts in all gas mixtures) [50,54]. On both catalysts and in all reaction gas mixtures, the intensity of the bidentate formate related signals first increases for approximately 10 min, passes through a maximum and then decreases for the remaining reaction time.

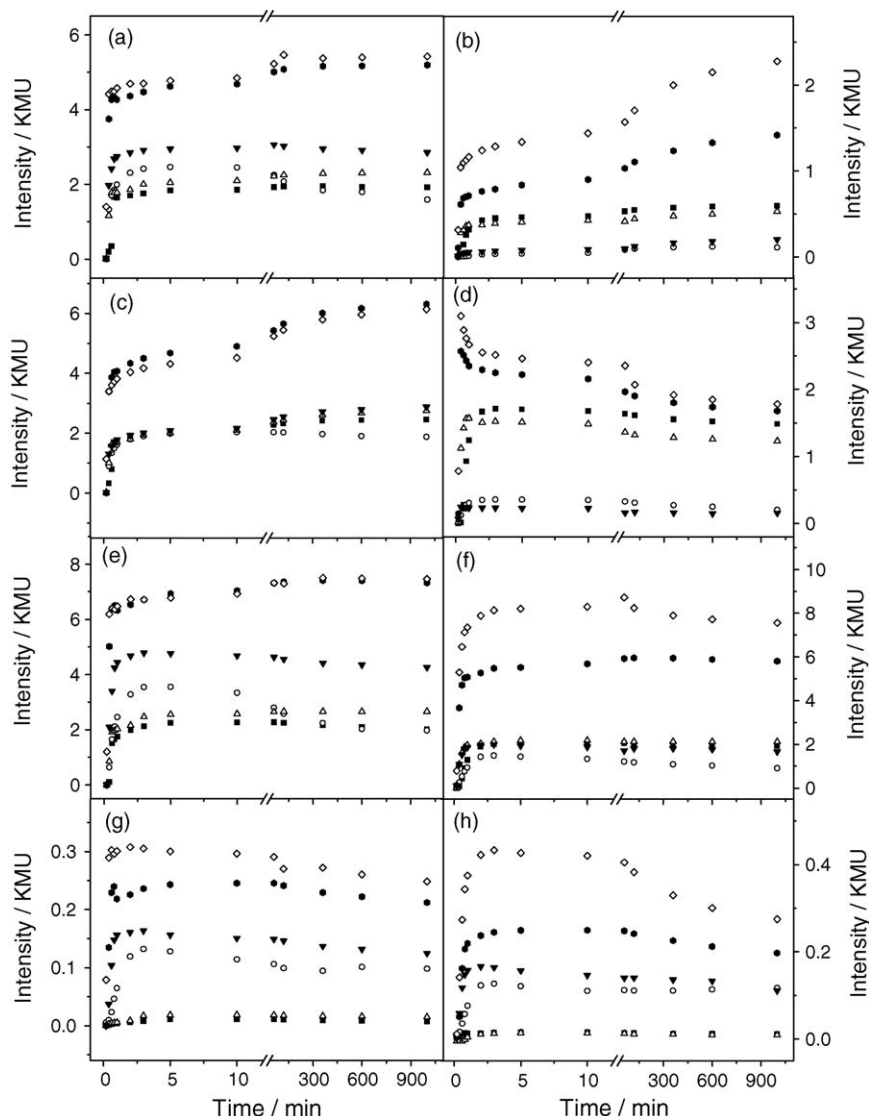


Fig. 5. Time evolution of the peak intensities (after normalization to similar reflectivities and background subtraction) of different peaks in the DRIFT spectra during the WGS reaction in different gas mixture on 4.5 wt.% Au/CeO₂ catalysts at 300 °C. (a) Monodentate carbonate intensity at 1368 cm⁻¹ (O400), (b) monodentate carbonate intensity at 1410 cm⁻¹ (H400), (c) carbonate peak 1522 cm⁻¹ (O400), (d) bidentate carbonate peak at 1283 cm⁻¹ (H400), (e) formate related intensity at 1582 cm⁻¹ (O400), (f) formate related intensity at 1585 cm⁻¹ (H400), (g) bidentate formate intensity at 2832 cm⁻¹ (O400), (h) bidentate formate intensity at 2828 cm⁻¹ (H400) (■) idealized reformat, (○) H₂-rich idealized reformat, (△) CO₂-containing idealized reformat, (▼) CO₂ + H₂-rich idealized reformat, (●) 1/4 realistic reformat, and (◇) 1/2 realistic reformat (gas compositions see Table 1).

In *H₂-rich reformat*, both in the absence or presence of CO₂ and for both catalysts, the decrease of the bidentate formate related bands after 10 min reaction is accompanied by the appearance and growth of a new band at 2926 cm⁻¹, which essentially grew in intensity until the end of the measurements. Furthermore, after 10 h reaction, the position of the remaining peaks at 2828–2830 and 1583–1588 cm⁻¹ was shifted to 2853 and 1556 cm⁻¹ (both catalysts), respectively. Following previous reports, we relate the shift in wave number to the onset of surface reduction (bidentate formates on Ce³⁺ instead of Ce⁴⁺ surface species) [29]. The resulting surface species was previously identified as a less active bidentate surface formate [29,50,52]. The newly formed band at 2926 cm⁻¹, which appears only in H₂-rich atmospheres, is tentatively attributed to bridge-bonded formate species on reduced Ce³⁺ and Ce³⁺/Ce⁴⁺ sites [50,52,53]. Also this species was identified as less reactive than the ‘reactive’ bidentate surface formate at ~2830 cm⁻¹ [29]. The formation of a less reactive surface formate species at the expense of the ‘reactive’ bidentate formate species in *H₂-rich idealized reformat* agrees well with the observations at 180 °C on a H230 catalyst [29].

In more realistic gas mixtures (1/4 or 1/2 realistic reformat), the bidentate formate related peaks were more intense compared to the other reaction gas mixture, independent of the catalyst pre-treatment. Most likely, this is related to the much higher CO contents in these gas mixtures (and possibly also to the higher CO₂ contents). Furthermore, higher formates intensities were always observed after reductive pre-treatment than after oxidative pre-treatment under similar reaction conditions.

3.2.3. CO_{ad}/CO₂ region

In the CO_{ad} region (2000–2200 cm⁻¹), a peak at 2117 cm⁻¹ appears on the O400 catalysts, which is usually attributed to CO adsorbed on Au [55–57]. In all cases, the signals increase in intensity for the first 5 min, and then remain about constant. Because of the high temperature, the steady-state CO_{ad} coverage and hence also the IR intensity are very low throughout the reaction. In all idealized gas mixtures, the intensities are of comparable order of magnitude. Only in the more realistic gas mixtures the signals are more intense, as expected from the higher

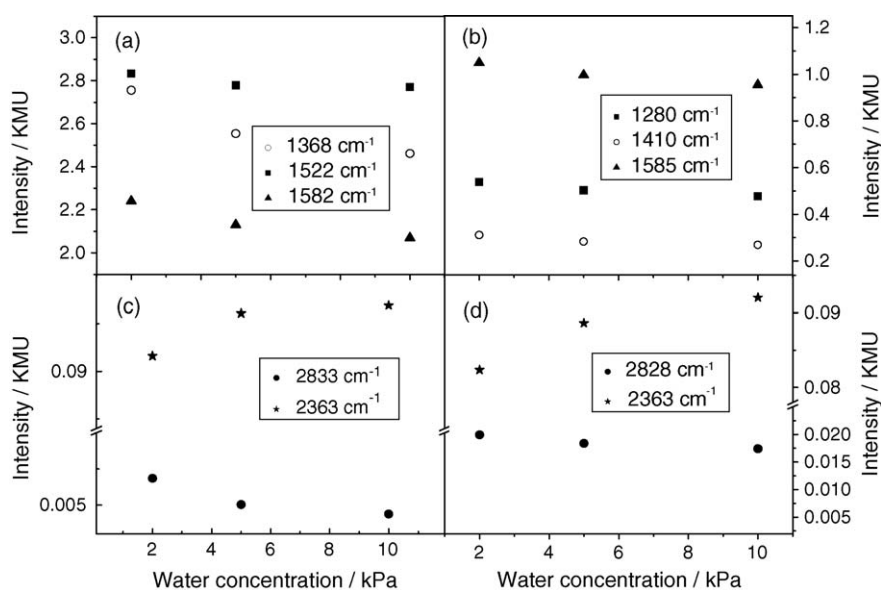


Fig. 6. Peak intensities (after normalization to similar reflectivities and background subtraction) of different peaks in the DRIFT spectra during reaction in idealized reformate using different amounts of water on a 4.5 wt.% Au/CeO₂ catalyst at 300 °C as a function of the water content. (a) monodentate carbonate peak at 1368 cm⁻¹, carbonate peak at 1522 cm⁻¹ and formate related peak at 1582 cm⁻¹ (O400), (b) monodentate carbonate peak at 1410 cm⁻¹, bidentate carbonate peak at 1280 cm⁻¹ and formate related peak at 1585 cm⁻¹ (H400), (c) CO₂ peak at 2363 cm⁻¹ and bidentate formate peak at 2832 cm⁻¹ (O400), (d) CO₂ peak at 2363 cm⁻¹ and bidentate formate peak at 2828 cm⁻¹ (H400).

CO partial pressures. The lower intensities for the CO_{ad} peak in idealized gas mixtures go along with a higher activity compared to realistic reformate.

On the H400 catalysts, the signal of linearly adsorbed CO_{ad} was even weaker than on the O400 catalyst, and hard to separate from a signal, which is attributed to an electronic transition from donor levels located near the conduction band such as Ce³⁺ or oxygen vacancies and which is present in the background spectra after the reductive pre-treatment [49]. The weaker intensity of the CO_{ad} band on the reductively pre-treated catalyst compared to the oxidatively pre-treated one resembles earlier findings by Karpenko et al. [24] and Abd El-Moemen et al. [32] for Au/CeO₂ catalyst and by Denkwitz et al. for a Au/TiO₂ catalyst [58], and may be due to a co-adsorbate induced lowering of the adsorption energy and/or due to site blocking. The peak maximum appears at ~2120 cm⁻¹, independent of the gas mixture, with the peak extending to 2050 cm⁻¹. The up-shift in the presence of H₂ also resembles earlier findings [24,32,58], it may arise from the lower CO_{ad} coverage [56] or from adsorbate–adsorbate interactions.

3.2.4. OCO bending region (1200–1600 cm⁻¹)

The various bands in the OCO region arise from different surface carbonates, formates and carboxylates. Their exact positions depend only on the pre-treatments, while the intensities vary also between different gas mixtures. On the H400 catalysts, peaks related to surface carbonates appear at 1540 cm⁻¹ (shoulder, unspecified carbonate [48]), 1410–1415 cm⁻¹ (monodentate carbonate [48]) and 1283 cm⁻¹ (bidentate carbonate [48]). The first two peaks grow rapidly in intensity at the beginning of the reaction in *idealized reformate* and in *H₂O-rich idealized reformate*, where they reach their maximum value after 30 min, and then remain about constant. In *CO₂-containing idealized reformate* and in *H₂-rich idealized reformate*, the band at 1540 cm⁻¹ is small and hardly detectable, while that at 1414–1419 cm⁻¹ increased slightly in intensity during the first 10 min and remained constant afterwards. This closely resembles the behavior of the 1540 cm⁻¹ and 1410–1415 cm⁻¹ signals in the previous gas mixtures (*idealized reformate* and *H₂O-rich idealized reformate*). In more realistic reformate, the signal intensities followed similar trends, but the total intensity was significantly higher (and higher for 1/2

than for 1/4 *realistic reformate*). In this case, the intensity continued to grow also after the steep initial increase.

The bidentate carbonate signal increased rapidly in intensity, passed through a maximum after ~30 min, which is more or less pronounced depending on the gas mixtures, and then decreased gradually until the end of the reaction. This general behavior was observed in all reaction gas mixtures. Finally, the time-dependent behavior of the bidentate formate related peak at 1585 cm⁻¹ resembled that of the formate related C–H vibration at 2828 cm⁻¹.

Comparing the deactivation with time and the absolute values of the initial/final activities in the different reaction mixtures (Fig. 1) with the time-dependence of the bidentate carbonate intensity and the absolute intensity of this signal (Figs. 3 and 4), the following trends can be extracted. The highest bidentate carbonate intensity is found for the more realistic reformates, which also have the lowest activity. Furthermore, in these gas mixtures the deactivation is lowest, and at the same time the bidentate carbonate signal decreases with time after having passed through an initial maximum. In H₂-rich gas mixtures, the bidentate carbonate signal is very low and essentially constant with time. On the other hand, the activity in the H₂-rich reformate is in the medium range, while that of the CO₂ + H₂-rich *idealized reformate* is much lower (~20% of that in H₂-rich *reformate*), and one of the lowest among the different gas mixtures.

A similar comparison for the monodentate carbonate results in the following trends: similar to the bidentate carbonate, the highest monodentate intensity is obtained on the more realistic reformates, which correlates with the lowest activity in these gas mixtures. In this case, however, the intensity increases over the entire reaction time, while the deactivation is lowest among all reaction gas mixtures. In idealized reformates, where the deactivation is more pronounced, the increase of the monodentate carbonate signal is much less. In H₂-rich mixtures, also the monodentate carbonate intensities are lowest, while the activity in these mixtures is 70% of that in *idealized reformate* (for H₂-rich *reformate*) or much lower than that (for CO₂ + H₂-rich *idealized reformate*). Finally, for formates the trends are similar to those discussed for the C–H signal intensity above. In total, there are correlations between activity/deactivation on the one hand and carbonate signal intensity on the other hand in different reaction

atmospheres, but these are more complex than a simple correlation between (decreasing) activity and (increasing) surface carbonate coverage.

For the O400 catalysts, the peak positions are slightly different: the 'carbonate' related signal appears at $1522\text{--}1525\text{ cm}^{-1}$, that of monodentate carbonate at $1365\text{--}1369\text{ cm}^{-1}$, and the bidentate carbonate related signal, which was generally less intense than on the H400 catalyst, is located at $1302\text{--}1310\text{ cm}^{-1}$. The latter signal mostly appears only as a shoulder in the monodentate carbonate signal. The behavior of the carbonate and bidentate carbonate related peak intensities with time in *idealized reformat* and in CO_2 -containing *reformat* largely resembles that on the H400 catalyst in the corresponding reaction atmospheres, with a steep initial growth and a slow subsequent decay, only with different intensities. In the presence of H_2 , in H_2 -rich *idealized reformat* and in $\text{CO}_2 + \text{H}_2$ -rich *idealized reformat*, the intensity of the 'carbonate' related signal at $1522\text{--}1524\text{ cm}^{-1}$ remained essentially constant with time. The bidentate carbonate signal intensity first increased (~ 10 min) and then decreased and cannot be resolved any more after 1 h reaction time. The intensity of the monodentate carbonate signal was significantly higher on the O400 than on the H400 catalyst, independent of the reaction gas mixture. On the O400 catalyst, the lowest intensity of the monodentate carbonate related signals was observed in *idealized reformat* during almost all of the reaction time, with about constant intensity. Only at the very end the decreasing signal in H_2 -rich *idealized reformat* became even lower. In CO_2 -rich *reformat* and in $\text{CO}_2 + \text{H}_2$ -rich *reformat* the intensities were about 50% higher. In all cases, the signal increased steeply at the beginning of the reaction and then remained about constant. For the unspecified carbonates, which appeared as a pronounced peak on the O400 catalyst, the trends are like those described above for monodentate carbonate, and also the absolute intensities were of comparable order of magnitude (on the H400 catalyst the signal related to these carbonates was a hardly resolved shoulder on the formate signal).

Similar to the H400 catalyst, the highest amounts of carbonate species (all carbonate species) were obtained in the more realistic reformates. They are present already in the first spectrum recorded after starting the reaction (recorded 12–24 s), again similar to observations on the H400 catalyst, indicating that these species must have formed rapidly during the initial 20 s of the reaction. (Note that the background spectra recorded before the reaction showed much less carbonate species than in the above spectrum). After the initial steep increase, the signals of monodentate and of unspecified carbonate continued to grow in intensity, but the growth was much less pronounced than on the H400 catalyst. The total intensity, however, was higher on the O400 than on the H400 catalyst. The much weaker signals of the bidentate increased also initially (for ~ 10 min), but then remain about constant.

Similar to the H400 catalyst, we finally compare the deactivation with time and the absolute values of the initial/final activities in the different reaction mixtures with the time-dependence of the different carbonate signals. Because of the low intensity, we will omit the bidentate carbonate signal. Going to the monodentate carbonates, also on the O400 catalyst, the highest monodentate intensity in the more realistic reformates correlates well with the low activity in these gas mixtures (lowest activity among the different gas mixtures). Different from H400, however, the intensity is about constant in the later stages of the reaction, in good agreement with the more pronounced deactivation than on the H400 catalyst. In *idealized reformates*, where the deactivation is more pronounced, the monodentate carbonate signal is approximately constant. In H_2 -rich mixtures, we find the same behavior as on the H400

catalyst, with lowest monodentate carbonate intensities of all mixtures, but activities of 30% of that in *idealized reformat* (for H_2 -rich *reformat*) or much lower than that (for $\text{CO}_2 + \text{H}_2$ -rich *idealized reformat*). For unspecified carbonates, the trends are similar as for monodentate carbonates. Finally, for formates the trends are similar to those discussed for the C–H signal intensity above.

The increase in stability with temperature ($180 \rightarrow 300\text{ }^\circ\text{C}$) observed for the more realistic reformates as compared to the decrease in the stability for *idealized reformat* (and also the other *idealized reformates*) is accompanied also by a reversal of the monodentate carbonate growth during reaction. For reaction at $180\text{ }^\circ\text{C}$, the increase in monodentate carbonate is much higher for $1/2$ *realistic reformat* (239%) than for *idealized reformat* (134%) [29], while at $300\text{ }^\circ\text{C}$, the increase is much larger in *idealized reformat* than in $1/2$ *realistic reformat* (Fig. 5), although the total amount of surface carbonates is much higher in $1/2$ *realistic reformat*, which may be partly responsible for the much lower absolute activity in the latter gas mixture. These results also clearly underline the important role played by monodentate carbonates in the catalyst deactivation. For the underlying reason one may speculate that the lower decrease in carbonate coverage at $300\text{ }^\circ\text{C}$ in $1/2$ *realistic reformat* relative to *idealized reformat* may be due to an enhanced H_2O assisted decomposition of the surface carbonate species.

In total, the observations for the O400 catalyst lead to similar conclusions as for the H400 catalysts. There are qualitative correlations between the amount of carbonates present on the surface and the activity/deactivation, but these are not consistent for the all different gas mixtures. Mostly, the time-dependent increase of the carbonate signal does not correlate quantitatively with the deactivation. Hence, there is no simple correlation between (decreasing) activity and (increasing) surface carbonate coverage, and the deactivation is not solely related to the formation of surface carbonate species. Other effects, such as the reduction of Au^{3+} species [31] or the detachment of Au nanoparticles from the support [34] may contribute in addition (for further discussion see also Section 3.1.4 and over next section).

On the other hand, for both types of catalysts, the lowest amount of bidentate formate species was observed in *idealized reformat*, and it increases in the order:

$$\begin{aligned} \text{idealized reformat} &\approx \text{CO}_2 \text{ containing idealized reformat} \\ &< \text{H}_2\text{-rich idealized reformat} \approx \text{CO}_2 + \text{H}_2\text{-rich idealized} \\ &\text{reformat} < 1/4 \text{ realistic reformat} < 1/2 \text{ realistic reformat} \end{aligned}$$

both for the O400 and the H400 catalyst, respectively. This agrees well with the similar order of decreasing activity, at least on a qualitative scale, underlining the important role of bidentate formate species in the reaction. Also in this case, however, there is no simple correlation between bidentate formate coverage (intensity) and activity, since the time dependences in formate intensity and activity do not agree quantitatively for similar reaction gas mixtures. It should be noted that Meunier et al. could show that at temperatures between 100 and $150\text{ }^\circ\text{C}$ the formation and decomposition of IR visible formates contributes only little to CO_2 formation and hence represents a minority pathway for the WGS reaction under these conditions. The contribution of this pathway, however, increased significantly with temperature, and it is reasonable to assume that at the much higher reaction temperature of this study ($300\text{ }^\circ\text{C}$), this pathway will contribute significantly to the reaction. This assumption is supported by the qualitative correlation between formate intensity and reactivity for different reaction mixtures. The actual contribution of this pathway is likely to vary with the reaction atmosphere, causing the discrepancies in the quantitative correlation.

3.3. Comparison with 180 °C reaction temperature

Comparing our results with the reaction at 180 °C shows that qualitatively the trends in the temporal evolution of the OH, surface formate, surface carbonate and CO₂ related signal intensities are similar in both cases. The formate intensity is lower at 300 °C than at 180 °C. On the other hand, the absolute carbonate intensity is higher at 300 °C reaction temperature, paralleling the stronger deactivation under these conditions [24,29,32]. The bidentate formate intensity first passes through an initial maximum at ~10 min and then decreases, independent of the pre-treatment and reaction gas mixture. The lowest intensity of the bidentate formate signal after 1000 min reaction was observed in *idealized reformat*, the highest in 1/2 *realistic reformat*, which agrees with the steady-state reaction activities. Hence, similar as for the behavior in *idealized reformat* with increasing water contents (see next section), also here the steady-state bidentate formate signal intensities are at least qualitatively correlated with the activities, lending further credibility to the proposal that under present reaction conditions formation and decomposition of bidentate formates contributes significantly to the reaction. In that case, these species act as reaction intermediate in a major reaction pathway and their formation/decomposition represents the rate limiting step in this pathway (see also ref. [26]).

3.4. Effect of water content in idealized reformat

For a more quantitative explanation of the effect of different water contents on the catalytic behavior of the O400 and H400 pre-treated catalysts in *idealized reformat*, we plotted the intensities at the end of the reaction (~steady-state intensities) vs. the water content in the reaction atmosphere (Fig. 6). Independent of the catalyst pre-treatment, the amount of adsorbed carbonate species on the catalyst surface in the *idealized reformat* gas mixture decreased with increasing water content. This agrees well with the increasing activity and stability of the catalyst during WGS reaction, which, as described in Section 3.1.2, increased with increasing water content. The close correlation between carbonate coverage and activity also under steady-state conditions fits well to results in previous studies, where these carbonate species were proposed as a main cause for the deactivation of Au/CeO₂ catalysts during the WGS reaction [16,23,29,31,32]. Simple and clear cut proof of the role of surface carbonates in the deactivation process was provided by Karpenko et al. [31] and Abd El-Moemen et al. [32], who could show that after 1000 min on stream and subsequent re-conditioning of the Au/CeO₂ catalyst by O400 treatment, the carbonate bands were removed and the initial activity was essentially fully regained. Furthermore, also the signal intensity of bidentate surface formates decreased with increasing water content, while the CO₂ intensity increased, corresponding to an increase in activity. These observations are in line with a faster formate decomposition, and compatible with the proposal that formate species act as reaction intermediate in the dominant pathway of the WGS reaction under these conditions [26,29,31].

4. Summary and conclusions

The effect of H₂O, H₂ and CO₂ in the reaction gas mixture on the activity and deactivation behavior of oxidatively or reductively pre-treated 4.5 wt.% Au/CeO₂ catalysts in the WGS reaction at 300 °C was systematically investigated by kinetic and *in situ* DRIFTS measurements in a variety of gas mixture, going stepwise from idealized reformat to more realistic gas mixtures. The main results can be summarized as follows:

- (1) The pre-treatment has a significant influence on both activity and stability of the catalyst in the WGS reaction under these

conditions, independent of the reaction gas mixtures. Oxidative pre-treatment (O400) leads to a higher activity compared to pre-treatment in a reductive atmosphere (H400), while for the stability the trend is opposite.

- (2) The catalyst activity decreased upon adding CO₂ and/or H₂ to idealized reformat for the O400 catalyst, and the lowest activity was obtained for the realistic reformates. For the H400 catalyst, the general trend was similar, with the exception that in CO₂ + H₂-rich reformat the activity was comparable to that in the realistic reformates. The stability of the O400 catalyst decreased in the order:

1/2 realistic reformat \approx 1/4 realistic reformat >
CO₂-containing idealized reformat > H₂-rich idealized
reformat \approx CO₂ + H₂-rich idealized reformat >
idealized reformat

For the H400 catalyst, the order of stability is almost identical with only one exception:

1/2 realistic reformat \approx 1/4 realistic reformat >
H₂-rich idealized reformat \approx CO₂ + H₂-rich idealized
reformat > CO₂-containing idealized reformat > idealized
reformat

- (3) Increasing the water concentration in *idealized reformat* (5 and 10 kPa) increased both activity and stability, for both the O400 and the H400 pre-treated catalysts. This was accompanied by a lower formation of monodentate carbonate species on the catalyst surface.
- (4) Changing the reaction temperature from 180 to 300 °C leads to considerable changes in both activity and stability of the catalyst. Furthermore, these changes depend also on the composition of the reaction gas mixtures. For instance, at 180 °C, the catalyst was most stable in *idealized reformat* and also showed the highest activity, whereas for reaction at 300 °C the stability was lowest and the activity was highest in this reaction gas mixture (both O400 and H400, without considering H₂O-rich reformates). In general, however, the stability decreased (increasing deactivation) for the O400 and or remained at comparable order of magnitude for the H400 catalyst, when going to 300 °C. There is, however, one clear exception, which is important also from a practical point of view: in realistic reformates the stability is distinctly higher at 300 °C than at 180 °C, with ~10% (H400–300 °C) and ~35–40% (O400) deactivation over 1000 min reaction compared to 55–60% deactivation at 180 °C. It needs to be kept in mind, however, that also the pre-treatment temperature (230 °C) was different for the catalyst used in the 180 °C reaction measurements. Nevertheless, in realistic reaction mixtures, the higher reaction temperature does indeed enhance the catalyst stability, different from the behavior in idealized reformates [32]. This is correlated with a similar reversal in surface carbonate build-up during reaction, which in idealized reformates is more pronounced at 300 °C than at 180 °C, while for the more realistic reformates this is opposite, underlining the importance of surface carbonates for the deactivation of these catalysts.
- (5) The DRIFTS measurements during the WGS reaction in idealized and also more realistic reformates show the same adsorbed reaction intermediate and side products, independent of the pre-treatments, although with different intensities. This supports the idea that the reaction pathway is not changed by the presence of CO₂, H₂, and/or different H₂O concentrations, although the presence of or change in short-living reaction intermediates can in principle not be ruled out. The same also holds true for different reaction temperatures of 180

and 300 °C. The distinct differences in activity and stability mainly arise from the very different coverages of the respective surface species under reaction conditions.

- (6) High H₂ partial pressures lead to a partial reduction of the support, modifying the adsorption sites for surface species adsorbed on the support. Consequently, new formate species were formed on the catalyst surface, characterized by vibration bands at 2853 and 2962 cm⁻¹, which were not observed in H₂-free atmospheres and which were previously identified as less reactive reaction intermediates [29].
- (7) The stability of the Au/CeO₂ catalyst is considerably higher in H₂-rich atmosphere than in H₂-free atmosphere. Therefore, support over-reduction can be discarded as a main reason for deactivation during WGS reaction [33].
- (8) The deactivation behavior is more complex at 300 °C than at 180 °C. While at the lower temperature, there is a definite correlation between monodentate carbonate coverage and activity [29,31], the correlation is less clear for reaction at 300 °C. Therefore, the accumulation of surface carbonates can not be the sole reason for deactivation under these conditions, and other effects have to be considered as well.

Acknowledgement

Ayman Abd El-Moemen is grateful for a fellowship from the Ministry of Higher Education of Egypt within the Channel Program.

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